Development of High-Energy Cathode Materials

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Pacific Northwest National Laboratory

2017 DOE Vehicle Technologies Program Review
June 5-9, 2017

Project ID #ES056

Overview

Timeline

- Start date: Oct. 2015
- End date: Sept. 2018
- Percent complete: 50%

Barriers addressed

- Low energy / high cost
- Limited cycle life
- Safety

Budget

- Total project funding: $1.2M
  - DOE share: 100%
- Funding received in FY16: $400k
- Funding received in FY17: $350k

Partners

- Argonne National Laboratory
- Western University, CA
- Brookhaven National Laboratory
- Army Research Laboratory

Relevance/Objectives

- Optimize Ni-rich $LiNi_xMn_yCo_zO_2$ (NMC) cathode materials using controlled co-precipitation method.
- Identify surface lattice doping effect on the cycling stability of Ni-rich NMC at high charge cutoff voltage.
- Improve the cycling stability of NMC cathode materials through solid electrolyte surface modification.
- Use advanced characterization techniques to understand the stability of NMC cathodes before and after structural modification.

Milestones

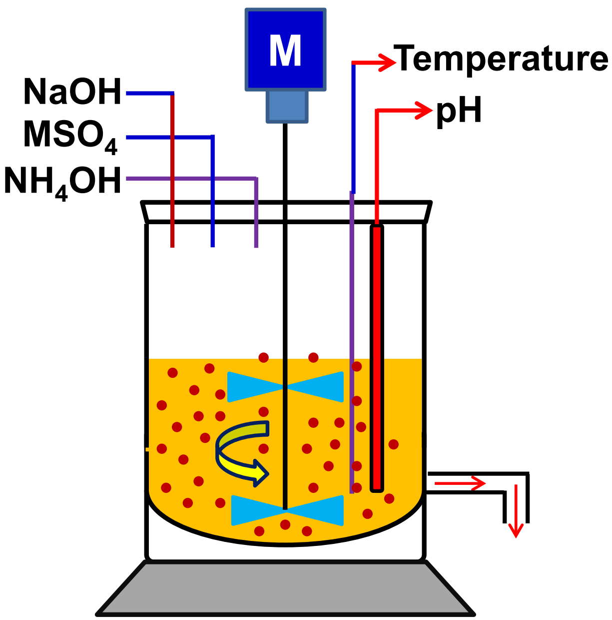
Date	Milestones and Go/No-Go Decisions	Status
Dec. 2016	Complete lattice doping to enhance the cycling stability of NMC at high charge cutoff voltages.	Completed
March 2017	Identify appropriate solvents for surface modification of NMC and reveal the structural changes after wash with water.	Completed
18-month Go/No Go	Capacity retention of 85% or higher after 150 cycles.	Completed
June 2017	Complete surface modification to enhance the cycling stability of NMC at high charge cutoff voltages.	Completed
Sept. 2017	Achieve NMC performance improvement of 200 mAh g^{-1} and 80% capacity retention after 200 cycles.	On going

Approach

1. Use controlled co-precipitation method (continuously stirred tank reactor) to synthesize the Ni-rich NMC cathodes with different compositions.
2. Optimize the doping elements and surface treatment approaches to enhance the stability of Ni-rich NMC cathode materials.
3. Use advanced microscopic characterizations to investigate the capacity improvement mechanism of solid electrolyte surface modification.

Technical Accomplishments

Optimize compositions of NMC materials to achieve improved electrochemical performance



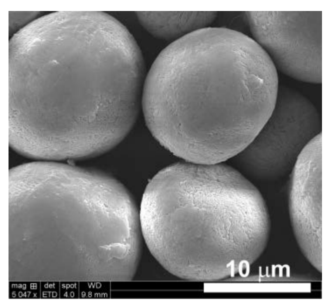
Synthesis conditions:

Flow rate; pH value; Tank volume;

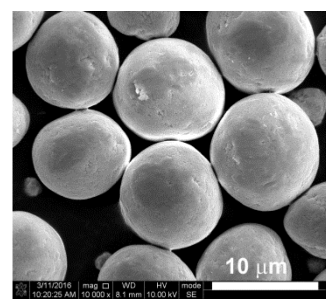
Concentration of NH_4OH and MSO_4/NaOH;

Temperature; Stirring speed

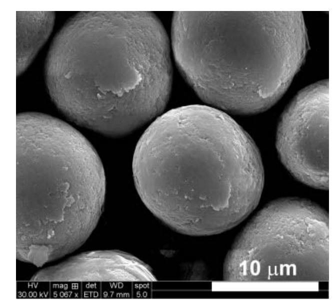
$Ni_{0.5}Mn_{0.3}Co_{0.2}(OH)_2$



$Ni_{0.68}Mn_{0.22}Co_{0.10}(OH)_2$



$Ni_{0.76}Mn_{0.14}Co_{0.10}(OH)_2$

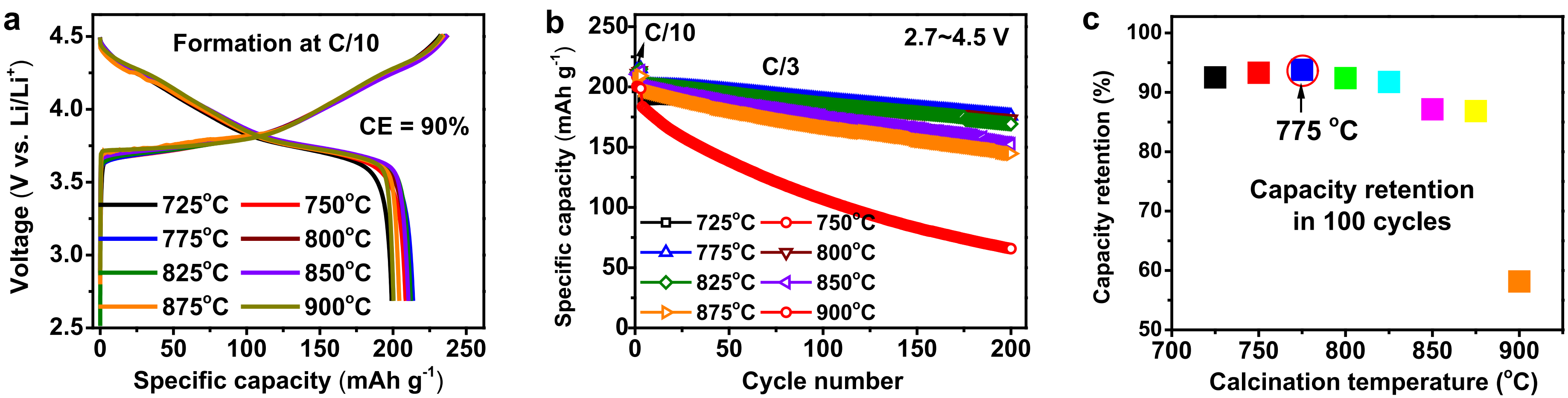


- Different NMC hydroxide precursors with average particle size of ca. 10 μm have been successfully synthesized.

Technical Accomplishments

Optimize compositions of NMC materials to achieve improved electrochemical performance

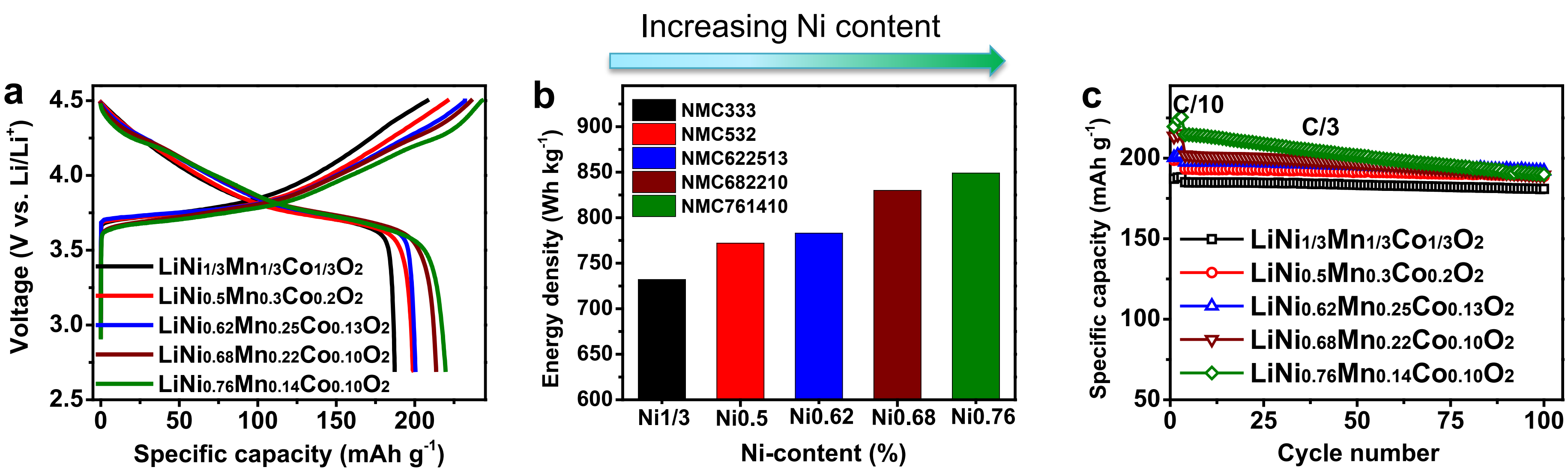
Calcination temperature effects on Ni-rich NMC: $LiNi_{0.68}Mn_{0.22}Co_{0.10}O_2$



- Long-term cycle life of Ni-rich cathode materials is very sensitive to calcination temperature.
- For instance, the optimal calcination temperature of a Ni-rich $LiNi_{0.68}Mn_{0.22}Co_{0.10}O_2$ is ca. 775°C.

Technical Accomplishments

Optimize compositions of NMC materials to achieve improved electrochemical performance



Ni content should be ≥ 0.6 to achieve:

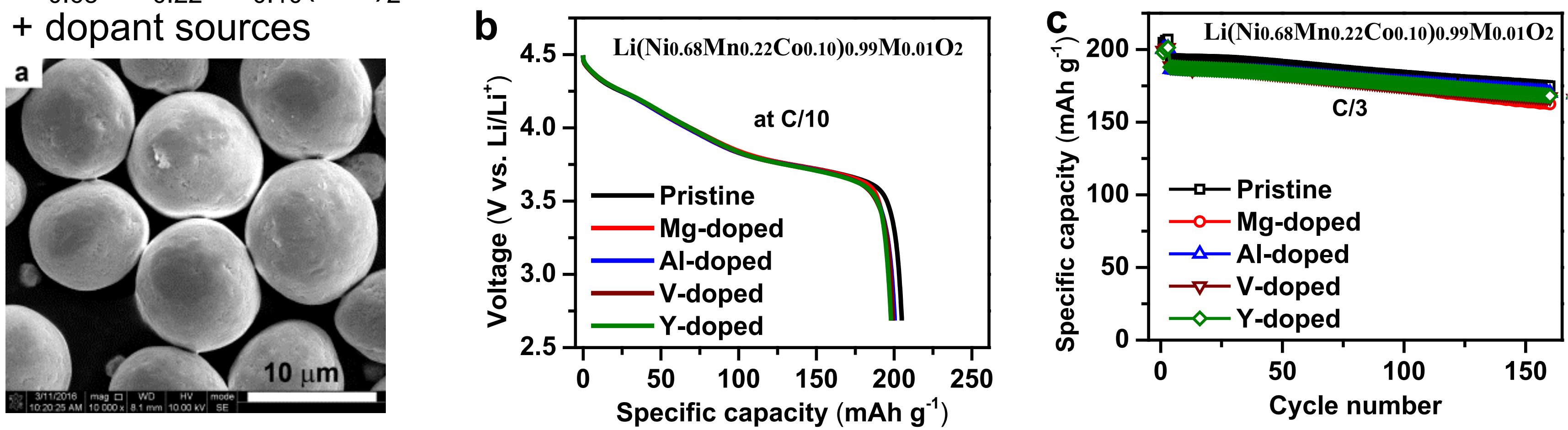
- capacity > 200 mAh g^{-1}
- energy density >800 Wh kg^{-1}

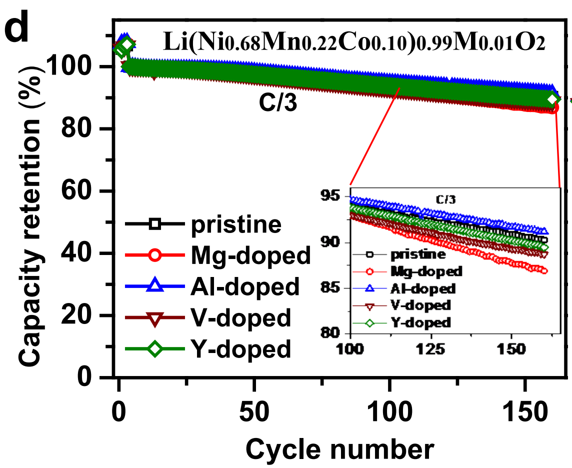
- Rising of Ni content in NMC cathodes leads to higher discharge capacity, but compromises the long-term cycling stability.

Technical Accomplishments

Surface lattice doping enhanced cycling stability of NMC cathode materials

$Ni_{0.68}Mn_{0.22}Co_{0.10}(OH)_2$
+ dopant sources





- ➢ The surface cation doping shows very limited effect, because it may not effectively suppress the secondary particle cracking at deep delithiation process.

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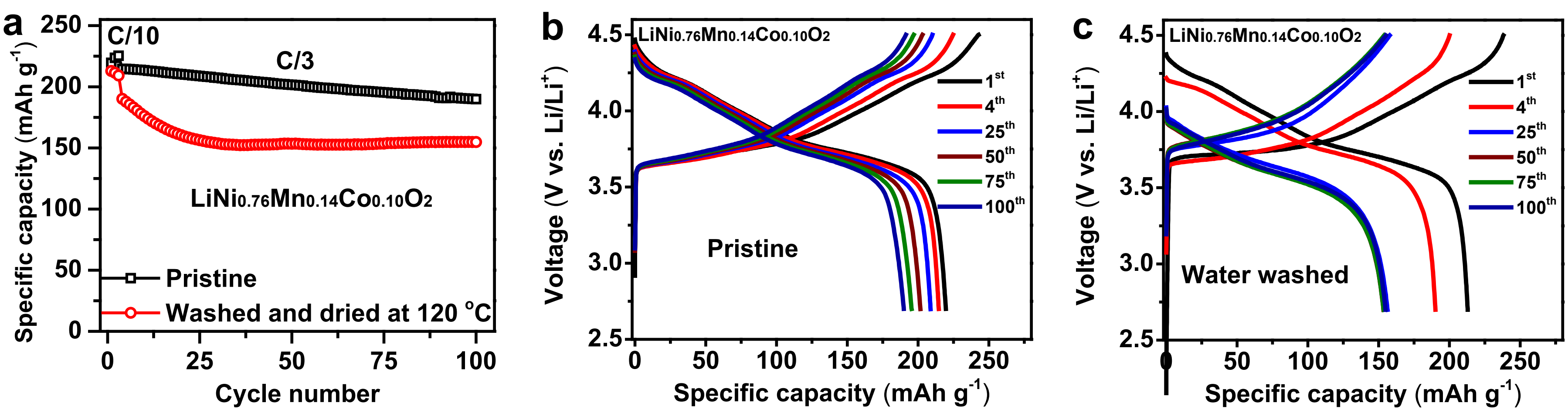
Technical Accomplishments

Performance degradation of NMC cathode materials after wash with water

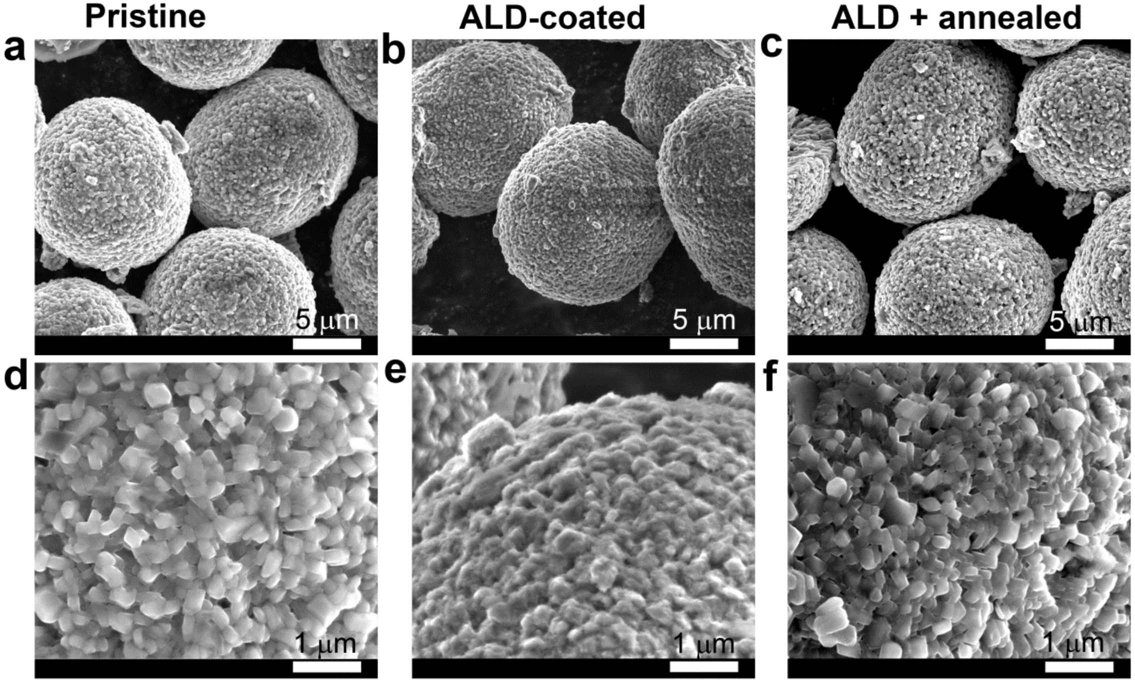


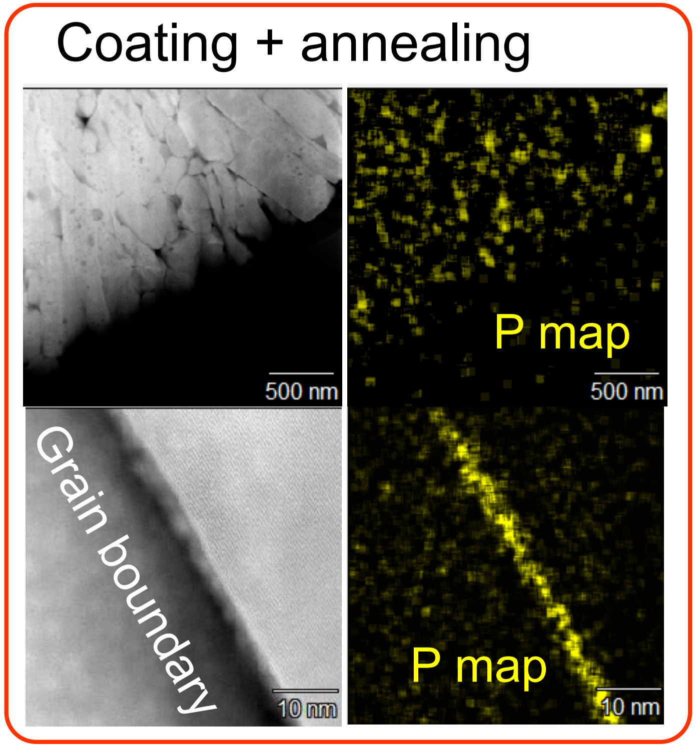
- ➢ Ni-rich NMC cathode materials are not stable with water.
- ➢ Surface treatment of Ni-rich NMCs should be performed in non-water environment, e.g. ALD method, etc.

Technical Accomplishments

Solid electrolyte modification enhanced cycling stability of NMC cathode materials

Ni-rich NMC: $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$

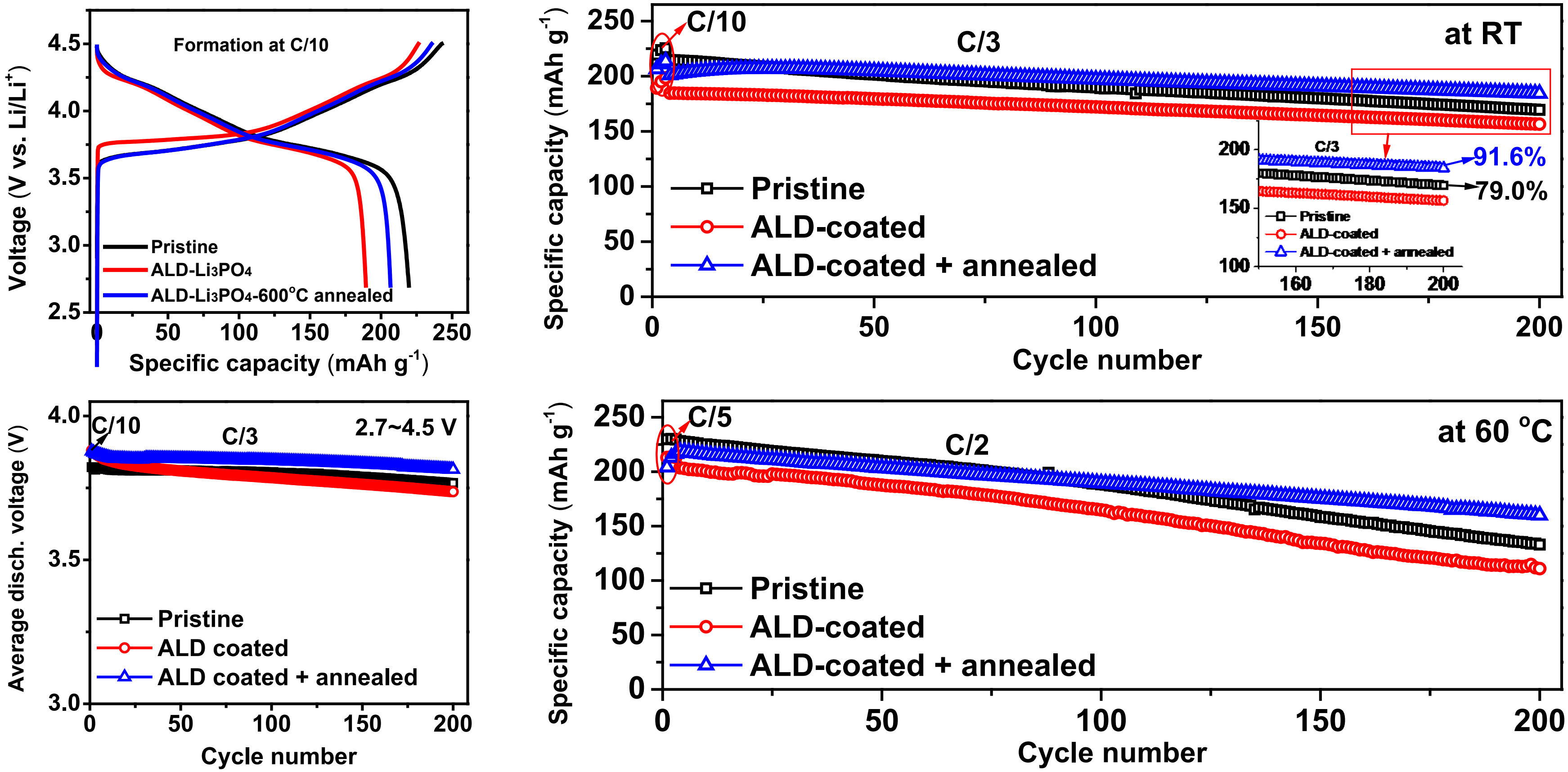




- Solid electrolyte Li_3PO_4 coating layer melts and diffuses inward, which uniformly coats on the surface of primary NMC particles.

Technical Accomplishments

Solid electrolyte modification enhanced cycling stability of NMC cathode materials

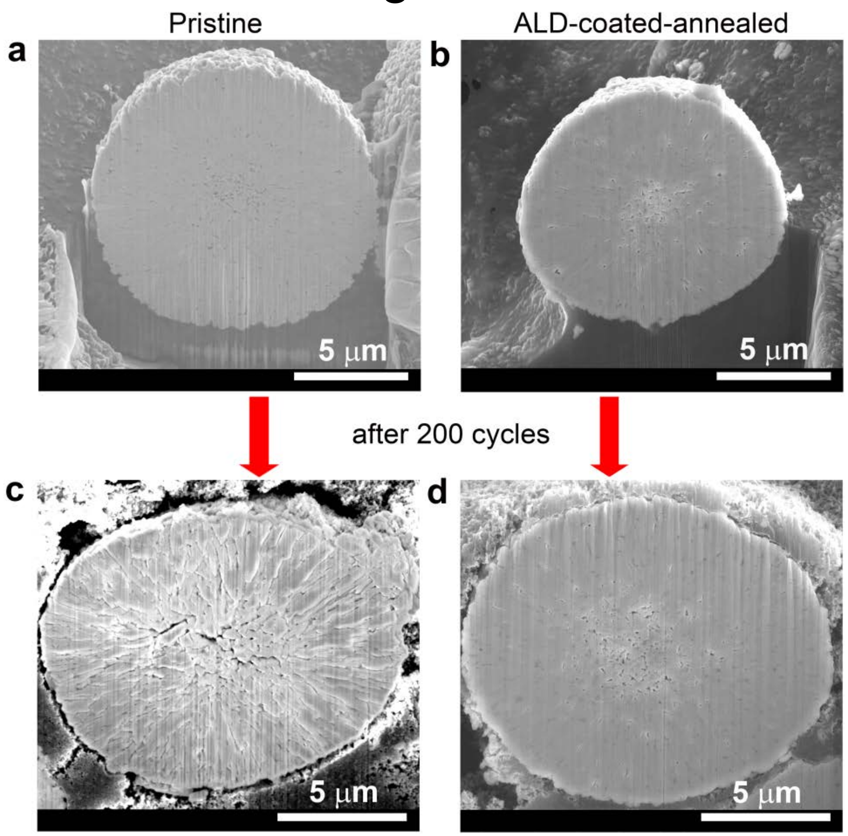


- Li_3PO_4-coated material show significantly improved cycling performance at both room temperature and 60°C.

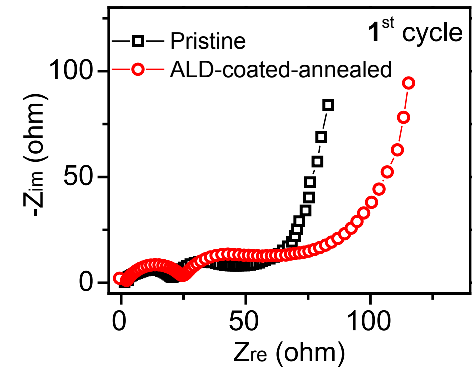
Technical Accomplishments

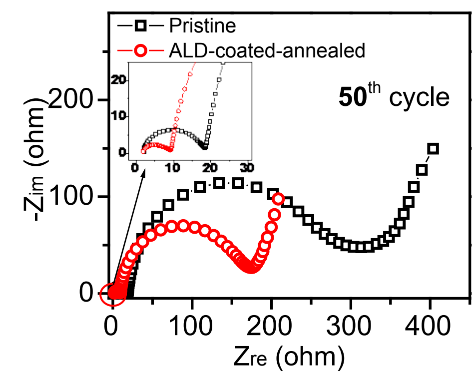
Solid electrolyte modification enhanced cycling stability of NMC cathode materials

Structural change



Interfacial evolution

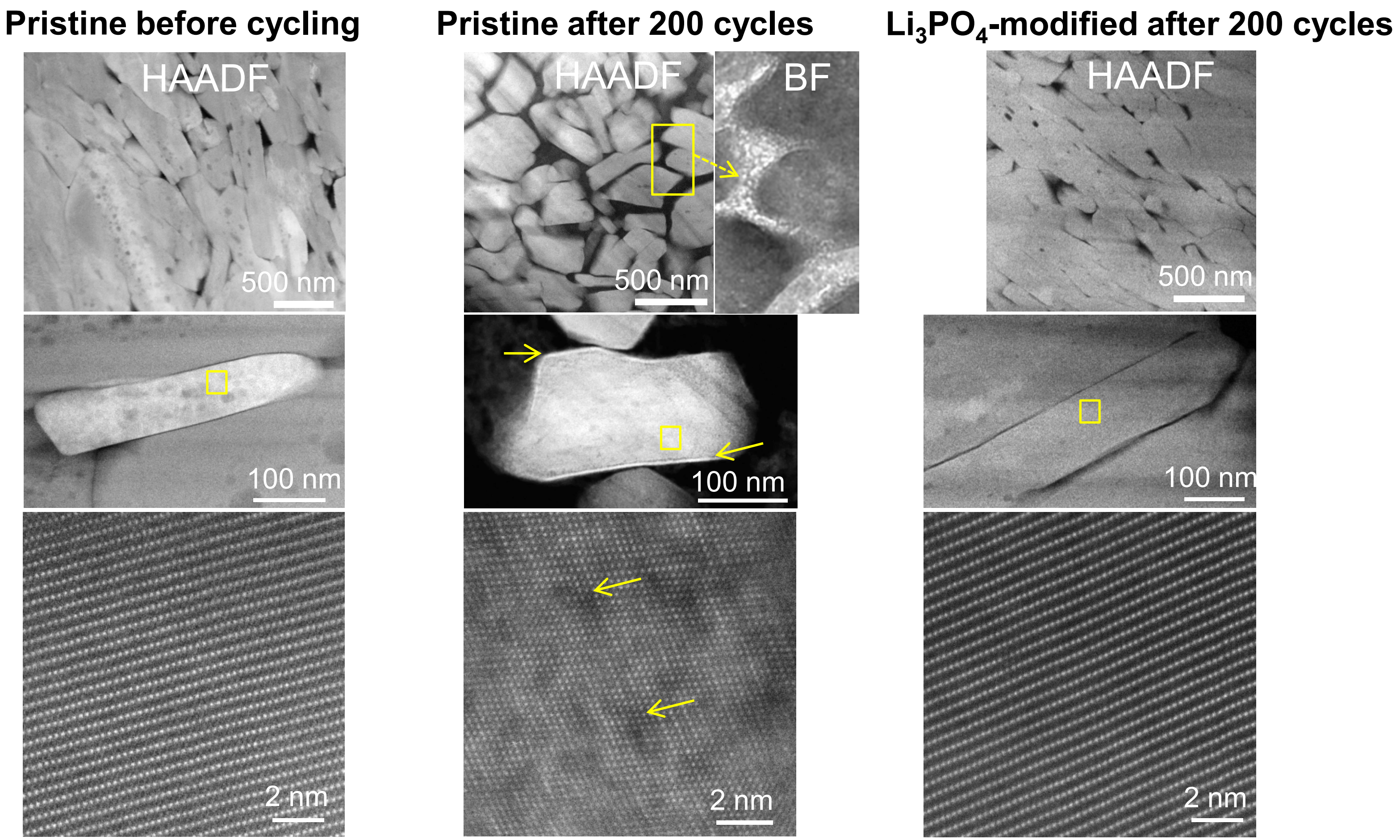




- Solid electrolyte Li_3PO_4-coating effectively improves the bulk structure and interfacial stability of Ni-rich NMC cathodes.

Technical Accomplishments

Solid electrolyte modification enhanced cycling stability of NMC cathode materials



- Solid electrolyte Li_3PO_4 treatment inhibits the structural degradation of Ni-rich NMC cathodes.

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Laboratory: provide standard NMC cathode and materials for testing.
- Western University, CA: ALD coating
- Brookhaven National Laboratory: *In situ* XRD on electrode materials.
- Army Research Laboratory: electrolytes and additives

Remaining Challenges and Barriers

- Ni-rich cathode materials deliver much higher discharge capacity (200~220 mAh g^{-1}), but their thermal stability still need to be improved.

- Although improved performance of Ni-rich NMC cathodes can be achieved in coin cells, their performances in graphite/NMC pouch cells still need to be further investigated.

Response to Reviewers' Comments

Project not reviewed in 2016

Proposed Future Research

- Complete the surface modification to improve the structural/interfacial stability of Ni-rich NMC cathodes. (on-going)
- Identify electrolyte additives to improve the interfacial stability of Ni-rich NMC cathodes. (proposed)
- Identify the structure and chemistry of SEI layer on NMC electrodes with different loadings using high sensitivity and high spatial resolution EDS mapping. (proposed)
- Validate the performance of NMC cathodes in graphite/NMC pouch cells, and optimize the structure and capacity matching of graphite/NMC pouch cells. (proposed)

Any proposed future work is subject to change based on funding levels.

Summary

1. Composition optimization of Ni-rich NMC cathode materials
   - Ni content needs to be higher than 0.6 to reach an initial discharge capacity of higher 200 mAh g^{-1}, but increasing Ni content also compromises the long-term cycling stability.
   - Ni-rich NMC with a composition of $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ exhibits a good combination of capacity and stability.

2. Surface lattice doping effects
   - Surface cation doping may not effectively suppress the secondary particle cracking at deep delithiation process, thus shows limited effect in improving the cycling stability of Ni-rich NMC.

3. Solid electrolyte coating enhanced performances of Ni-rich NMC cathode materials
   - Solid electrolyte Li_3PO_4 coating layer melts and diffuses inward during annealing process and forms a uniformly coating layer on the surface of <u>primary</u> NMC particles.
   - This solid electrolyte coating layer can effectively enhance the particle structural integrity and the interfacial stability, which improves the long-term cycling stability of Ni-rich NMC cathodes.

Acknowledgments

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- Team Members: Pengfei Yan, Wengao Zhao, Shuru Chen, Wu Xu, Chongmin Wang, Jun Liu

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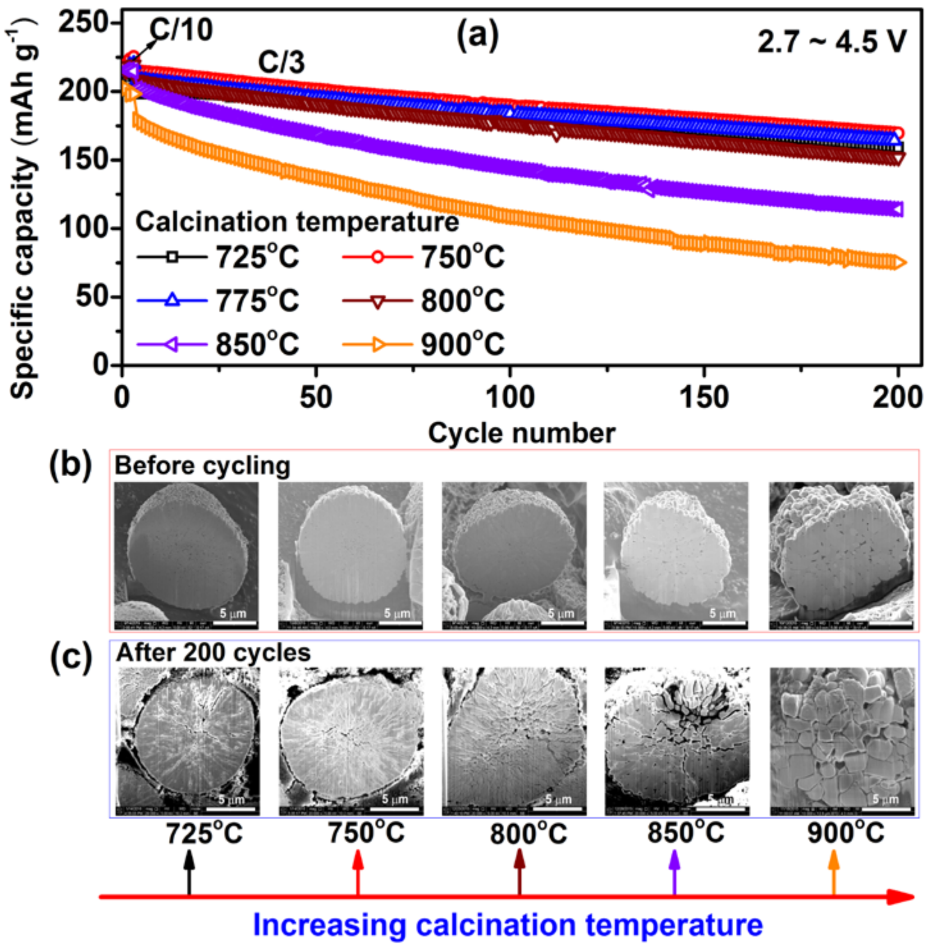
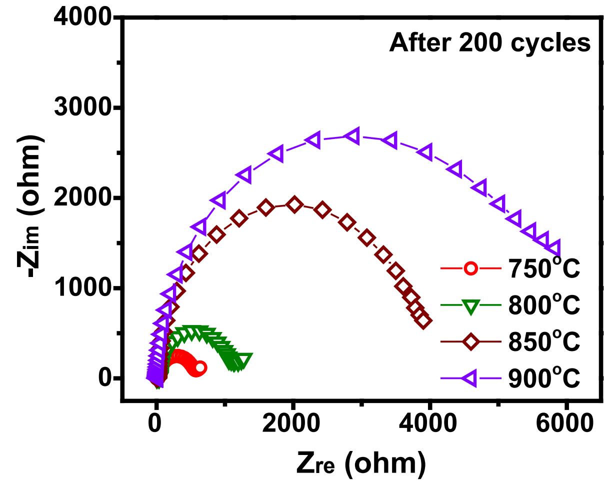
Technical Backup Slides

Technical Accomplishments

Capacity Degradation Mechanism of Ni-rich NMC materials calcined at different temperatures





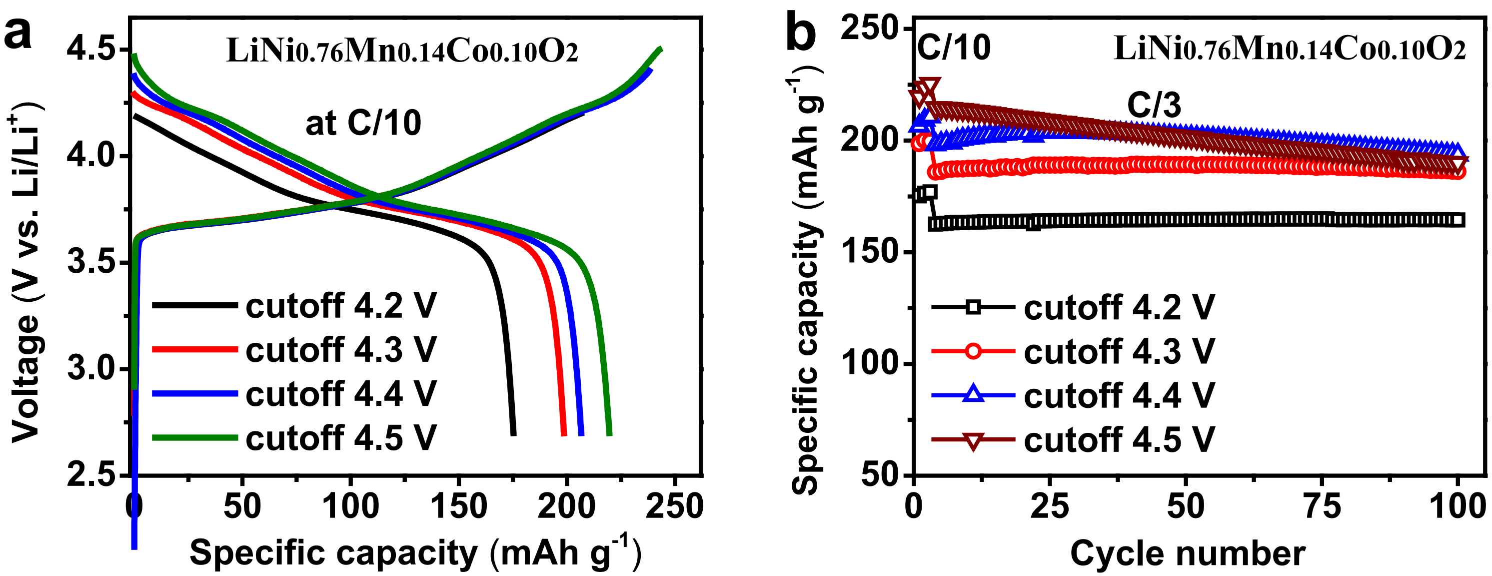
Origin for capacity degradation:

- ➢ Increase of internal strain
- ➢ **Particle cracking**
- ➢ Rapid built-up of charge transfer resistance.

Ni-rich $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$

Technical Accomplishments

Charge cut-off voltage effect on the cycling stability of Ni-rich NMC cathode materials



- Higher charge cutoff voltage leads to more extensive removal of lithium ions and the consequent structural/interfacial degradation.